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Push and pull: the potential role of boron in N₂ activation

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Recent developments in main group chemistry towards the activation and conversion of N₂ have led to the revelation that boron can greatly affect these processes. Boron is capable of acting both as a borane Lewis acid to activate metal–N₂ complexes and as an ambiphilic borylene able to activate free N₂. The latter example is capable of both accepting and donating electron density in a manner reminiscent of transition metal systems containing both filled and empty d-orbitals.

The functionalisation of N₂ remains one of the most persistent challenges in chemistry, even over a century since the advent of the Haber–Bosch process. This heterogeneous Fe catalyst remains the standard for the reduction of N₂ to NH₃. Chemists have been seeking alternatives to this energy intensive process for decades, however the development of commercially viable alternatives capable of breaking the remarkably strong NuN triple bond and enabling the subsequent reduction have remained elusive.

One approach to N₂ fixation has involved the use of homogeneous transition metal complexes to bind and ultimately functionalise N₂.¹ Such methods are inspired by nature, where nitrogenase enzymes employ Fe/Mo catalysts to fix N₂ at ambient temperatures and pressures.² Many approaches have been used to generate complexes capable of reacting with N₂, however a particularly successful method has been to develop low-valent transition metal complexes capable of binding and facilitating reactivity at the N₂ ligand.³ The efficacy of transition metal complexes in the binding of N₂ can be rationalised by the involvement of filled d-orbitals on the metal centre backdonating electron density into an antibonding π^* -orbital on the N₂ ligand (Fig. 1). This process renders the N₂ ligand activated and susceptible to further reactivity and functionalisation.

Recently, this process has been augmented by the use of the strong main group Lewis acid tris(pentafluorophenyl) borane [B(C₆F₅)₃].⁴ In conjunction with low-valent Fe, Mo and W centres, Szymczak⁵ and Simonneau⁶ were able to show that B(C₆F₅)₃ was able to increase greatly the degree of activation of the N₂ ligand in these M–N–N–B(C₆F₅)₃ complexes, as confirmed by IR measurements. The inclusion of B(C₆F₅)₃ into this system is thought to induce a “pull” effect resulting

in decreasing the bond order of the N₂ ligand, in conjunction with the “pushing” of electron density from the metal to the N₂ unit (Fig. 2). Furthermore, Szymczak has been able to show that the coordination of B(C₆F₅)₃ is able to protonate selectively the terminal N rather than the Fe centre when combined with the related HBAr^F₄. Absence of B(C₆F₅)₃ coordination results in Fe protonation, thus showing that B(C₆F₅)₃ results in a redistribution of electron density towards the terminal nitrogen atom.⁵

Conceptually, one can relate this type of reactivity to those of Frustrated Lewis Pairs (FLPs) where a Lewis acid and base react in a similar manner to activate small molecules. In recent years, FLPs and other main group systems have been shown to mimic the reactivity of a number of transition metal complexes, effectively mediating both stoichiometric and catalytic reactions that were once thought only possible for transition metal complexes.⁷ Such precedent has spawned the idea that main group complexes may well be potential alternatives to transition metal systems for the fixation of N₂.⁸ This Frontier article will focus on two recent examples where boron has been used to induce or mimic transition metal N₂ activation in different ways; one exploiting the high Lewis acidity of a borane and one the reactivity of cyclic alkyl(amino) carbene (CAAC) supported borylene complexes. These represent two different ideas of how boron can help facilitate the activation of N₂ one through ‘push’ type interactions where boron donates electron density to the N₂ unit and one through ‘pull’ type interactions driven by the Lewis acidity of electron deficient boranes.

As mentioned previously, the popular main group Lewis acid B(C₆F₅)₃ has been used to improve the degree of activation of N₂ in Fe, Mo, and W systems. In 2017, Stephan and co-workers reported on the reactivity of diphenyldiazomethane (Ph₂CNN) with B(C₆F₅)₃ and the related Lewis acid HB(C₆F₅)₂.⁹ The reactivity of diazo compounds is underexplored in main group chemistry despite their ubiquity in organic chemistry.

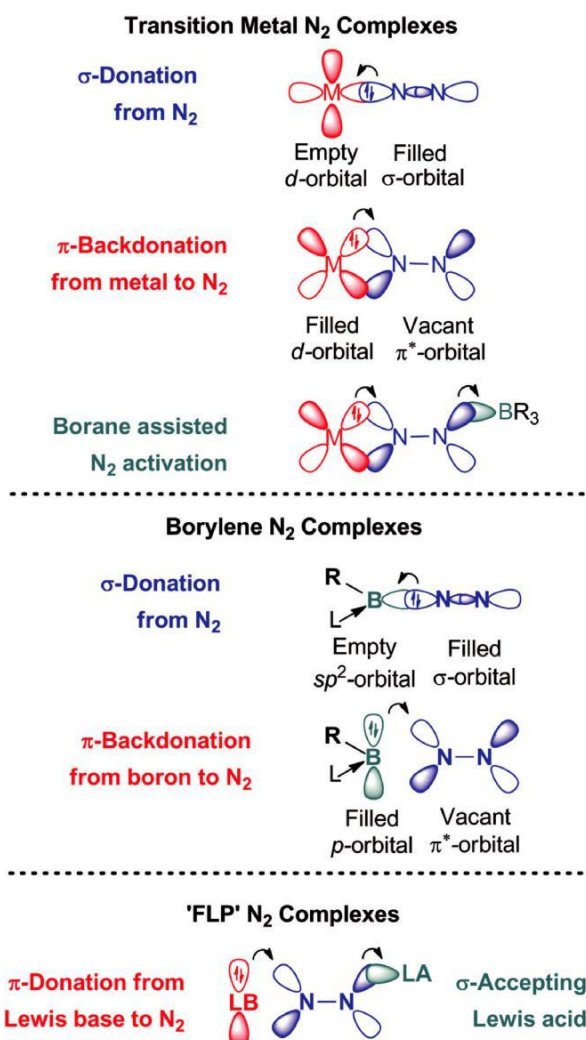


Fig. 1 Electronic configurations of transition metal and borylene N₂ complexes.

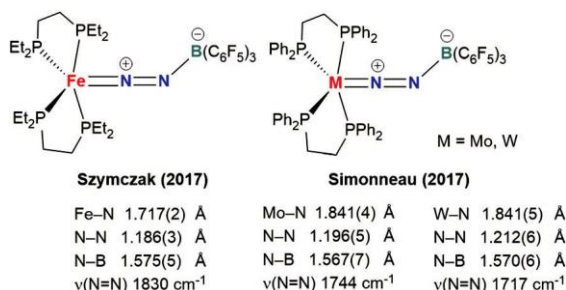
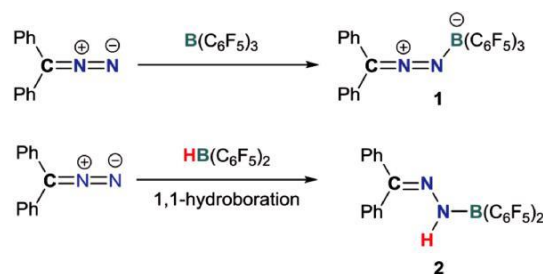


Fig. 2 Borane assisted N₂ activation at transition metal centres.

However, the insertion of diazo compounds into the B–C bonds of B(C₆F₅)₃ has been previously reported.¹⁰ When one considers the adduct between diphenyldiazomethane and a borane such as B(C₆F₅)₃, it can be interpreted as a system where N₂ has been trapped between a borane Lewis acid and a carbene Lewis base (Scheme 1). If such an adduct was to be



Scheme 1 Reactivity of diphenyldiazomethane with Lewis acidic boranes. 1: C–N 1.278(8) Å, N–N 1.177(7) Å, N–B 1.65(1) Å. 2: C–N 1.287(2) Å, N–N 1.3939(18) Å, N–B 1.385(2) Å.

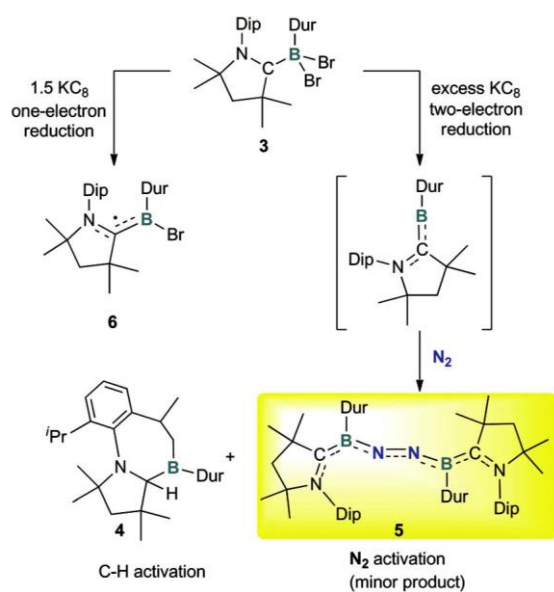
formed, one can imagine this as a template for how the product of an FLP mediated activation of N₂ may look.

Initial studies revealed that the adducts between diphenyldiazomethane and the Lewis acidic boranes B(C₆F₅)₃ was quite unstable and susceptible to the evolution of N₂ at room temperature. However, low temperature studies were able to uncover more information on the nature of this unstable adducts. Interestingly, the N–N bond length for the adduct of Ph₂CNN with B(C₆F₅)₃ was crystallographically determined to be in the range for those of N–N double bonds (and comparable to those reported for M–N–N–B(C₆F₅)₃ systems (M = Fe, Mo, W)).^{5,6} When Piers' borane, HB(C₆F₅)₂, was employed in this reaction, a 1,1-hydroboration of the N–N bond was observed to form complex 2. Such a reaction is in contrast to the more traditional 1,2-hydroborations typically observed. Two mechanisms were considered, direct 1,1-hydroboration or 1,2-hydroboration followed by a hydrogen shift. Computational analysis corroborated the latter proposal, indicating the formation of a 3-centre-2-electron-like early transition state between the B–H–N unit. Bond orders of 0.54 and 0.33 were calculated for the B–H and N–H bonds respectively.⁹ This type of interaction is indicative of donation of electron density from the B–H bond into a π^* -orbital on the N–N unit. Notably, this type of electron donation into a low-lying π^* -antibonding orbital is exactly how activation of N₂ is proposed to happen at transition metal centres.¹ The similar type of reactivity observed in this metal-free system is quite exciting, as one can envisage further modifications being made to facilitate subsequent reactivity at the N–N unit.

As an alternative to using main group compounds as Lewis acids, the chemistry of low-valent p-block compounds has been well studied in recent years.¹¹ Base-stabilised borylene complexes, monovalent boron stabilised by one or two neutral donors, represent one class of such compounds (Fig. 1).^{12,13} Containing filled and vacant orbitals at boron, such compounds represent ideal candidates for potential nitrogen fixation at a main group centre. The viability of such borylenes in N₂ activation has been highlighted by a recent study where the unstabilised borylene PhB: is able to bind N₂ under matrix conditions.¹⁴ This study suggests that borylenes contain the appropriate electronic structure to activate N₂, and with the proper choice of stabilising ligands, may be capable of fixing N₂ under mild conditions.

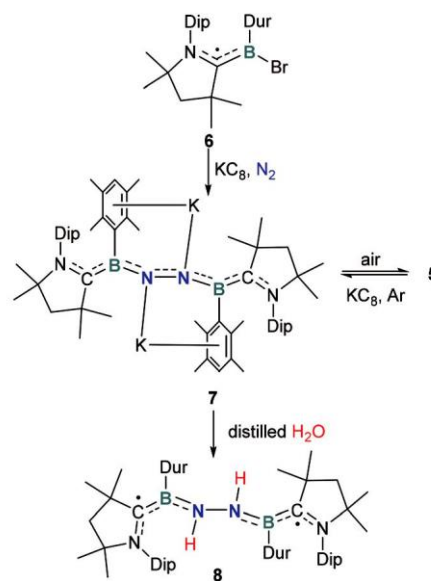
In this vein, the chemistry of borylene and borylene-like compounds stabilised by cyclic alkyl(amino) carbenes (CAAC) ligands has been reported by the groups of Bertrand, Stephan and Braunschweig.^{15–17} Among the reactivity studied by these groups, borylene complexes were shown to undergo carbon monoxide fixation, photolytic decarbonylation reactions, and ligand exchange reactions. The isoelectronic relationship of CO and N₂ suggests that such borylene complexes may be ideal candidates for nitrogen fixation at boron. These hypotheses were substantiated by the strong backbonding observed in borylene–CO complexes reported by Braunschweig and led to further studies of CAAC-stabilised borylene complexes as candidates for nitrogen fixation.¹⁸

Braunschweig and co-workers were previously able to show that the complex [(Dur)B(CO)(CAAC)] was able to undergo photolytic decarbonylation to form a transient [(Dur)B(CAAC)] species which was shown to complex Lewis bases (Dur = 2,3,5,6-tetramethylbenzene; CAAC = 1-(2,6-diisopropylphenyl)-3,3,5,5-tetramethylpyrrolidin-2-ylidene).^{16,17} In the absence of Lewis bases, [(Dur)B(CAAC)] was found to undergo an intra-molecular C–H activation reaction to form 4. Notably, attempts to decarbonylate [(Dur)B(CO)(CAAC)] under a N₂ atmosphere did not result in N₂ fixation, such reactions resulted in the isolation of the C–H activated species 4. The formation of [(Dur)B(CO)(CAAC)] proved to be initially inefficient, as the only synthesis involved the reaction of a CAAC with a Fe–borylene complex. Attempts to generate [(Dur)B(CO)(CAAC)] in a more efficient manner lead to the optimisation of a more stream-lined approach to its synthesis, where [(Dur)B(CAAC)Br₂] (3) could be simply reduced using excess KC₈ under a CO atmosphere (Scheme 2). If the reduction of 3 was performed in an argon atmosphere, the C–H activation product 4 was formed. However, when this reaction was performed at –80 °C under a N₂ atmosphere, a new fuchsia coloured species was seen.



Scheme 2 Reactivity of reduced [(Dur)B(CAAC)] fragment.

Upon analysis of the reaction mixture after warming to room temperature overnight, two diastereomers of the C–H activated product 4 were observed as the major species present. In addition, a small crop of dark purple crystals were isolated from the reaction mixture which had a shift of $\delta = 10.7$ ppm in the ¹¹B NMR spectrum, representing a species previously unseen in this chemistry. Remarkably, the dark purple crystals were found to be the product of N₂ fixation, 5, where N₂ has been trapped between two [(Dur)B(CAAC)] units (Scheme 2). Attempts to separate this species from 4 proved difficult, therefore another more selective synthetic route to 5 was investigated through the one electron reduction of radical species 6. Primary observations of the reaction indicated initial formation of the dark purple N₂ activation product 5, however upon warming to room temperature a colour change to dark blue was observed and the dipotassium complex 7 was formed (Scheme 3). This compound was able to be cleanly obtained from the reaction mixture and was isolated in a yield of 64%. The structures of 5 and 7 were analysed by crystallographic techniques. The structure of 5 proved to be unsymmetrical, whereas 7 was shown to contain an element of symmetry (Fig. 3). Notably, the N–N bond length in 5 was observed to be 1.248(4) Å, a value comparable with numerous organic N–N double bonds, and well short of those typically observed for N–N single bonds. The B–N–N–B torsion angle of 113.3(4)° is in contrast to the linear angle typically observed for similar transition metal M–N–N–M complexes.¹⁹ Such a difference in geometry can be rationalised by the orbitals available to participate in backbonding in each system. The p-orbitals of boron are not able to conform to the linear geometry observed in transition metal systems due to the participation of d-orbitals. Despite this difference in geometry, the borylene–nitrogen interaction is believed to resemble transition metal–N₂ com-



Scheme 3 Synthesis of N₂ fixation product 5 and hydrazine derivative 8.

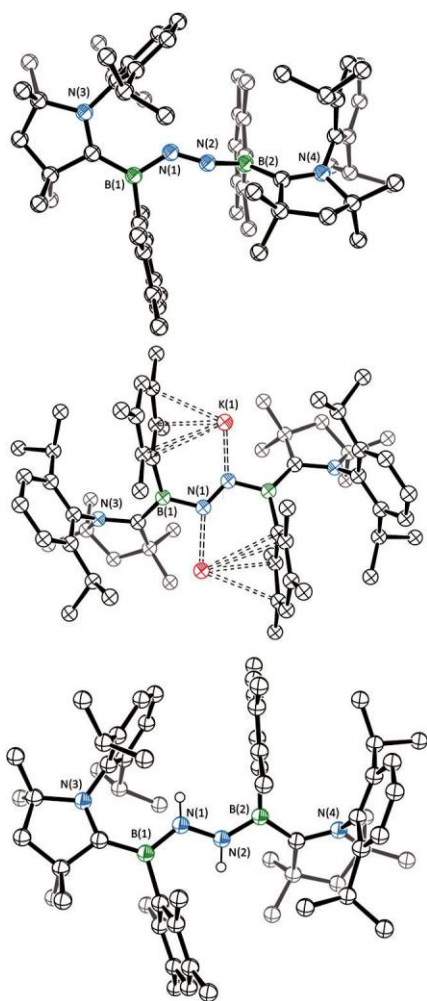


Fig. 3 Solid-state structures of 5 (top), 7 (middle), and 8 (bottom). Thermal ellipsoids are shown at 50% probability. 5: B(1)–N(1) 1.423(4) Å, N(1)–N(2) 1.248(4) Å, N(2)–B(2) 1.403(5) Å. 7: B(1)–N(1) 1.484(4) Å, N(1)–N(2) 1.304(4) Å, K(1)–N(2) 2.687(2) Å. 8: B(1)–N(1) 1.435(4) Å, N(1)–N(2) 1.402(2) Å, N(2)–B(2) 1.417(4) Å.

plexes rather than other more traditional organic N–N containing compounds.

The transition metal-like interaction in 5 can be seen in the short bonds observed between the carbene and borylene fragments (1.528(5) Å, 1.541(4) Å). The short distances resemble those witnessed in other CAAC supported monovalent borylene complexes,^{15–17} suggesting that the borylene in this system is acting as a σ -acceptor and π -donor to the N–N fragment. These observations were corroborated by DFT calculations, where Kohn–Sham orbital analysis confirmed the experimentally determined geometry and revealed the HOMO–1 contains an interaction between a boron p-orbital, N–N π^* -orbital, and carbene–N π^* -orbitals. This backdonation of electron density from boron to both the CAAC ligand and N₂ fragment strongly resembles the backdonation observed from filled d-orbitals on transition metals.

The solid-state structure of dipotassium complex 7 revealed a slightly different bonding motif to that observed in 5. Elongation of the B–N bonds and shortening of the carbene–B bonds are observed in 7, suggesting an increased degree of backbonding from the borylene to the CAAC ligand relative to the N₂ fragment. Such an observation was expected as the N–N orbitals in the reduced complex already contain extra electron density relative to 5, lessening the need of backdonation from boron.

When exposed to air, complex 7 was readily oxidised to the neutral N₂ compound 5 in good yield, providing a route for the reproducible isolation of 5. Similarly, if 5 is allowed to react with KC₈ under an argon atmosphere, regeneration of the dipotassium complex 7 is observed (Scheme 3). Reaction of 7 with distilled water resulted in the generation of a new Turquoise coloured species, revealed to be diradical species 8. The solid-state structure of 8 shows the formation of what is best described as a diborahydrazine complex. The N–N bond distance of 1.402(2) Å in this complex is well within the accepted region for that of a N–N single bond. The diradical nature of 8 was not surprising as a number of [(CAAC)BR₂[•]] radicals are known, and the experimental and spectroscopic data obtained for 8 agreed well with such compounds.²⁰

Complex 8 represents the first species isolated in this study containing a N–N single bond. This is quite significant as it suggests that, not only can N₂ be trapped between two borylene units, but this framework is capable of supporting the reduction of N₂ to a hydrazine derivative under mild reaction conditions. This reaction can be thought of as representing a partial reduction of N₂ to NH₃, and provides a platform for the further investigation of nitrogen fixation at main group centres.

Conclusions

As main group chemistry continues to search for similarities (and differences) that bridge the divide between transition metal chemistry and that of the p-block,²¹ the chemistry described in this Frontier article highlights the potential role of boron in the fixation of N₂. Boranes can facilitate this process by participating in both electron-withdrawing (“pull”) and electron-donating (“push”) types of interaction. Lewis acidic boranes had been previously shown to assist in the activation of N₂ in transition metal systems by ‘pulling’ on the N₂ ligand and facilitating N₂ activation. This chemistry was expanded to metal-free systems, where diazodiphenylmethane was used as a precursor for the isolation of a FLP-like species that would be the product of N₂ activation between a carbene and a borane. This result represented an exciting step forward in this field, as it demonstrated that the trapping of N₂ between two main group fragments was possible and that the Lewis acidic nature of boranes may be key to this process. However, such a system itself would not be capable of activation of N₂ gas.

Expanding this chemistry further, the landmark study published by Braunschweig represents a paradigm shift in this field, where boron, an element whose role in N₂ activation was thought to be to “pull” through its Lewis acidic nature was able to “push” electron density to N₂. This study revealed that, through the proper manipulation of the electronic structure at boron, borylene species containing both filled and empty orbitals are competent in the fixation of N₂, mimicking the reactivity exhibited by transition metals. Furthermore, the fixed nitrogen was reduced to a hydrazine derivative using water, demonstrating the exciting ability for such species to not only coordinate N₂, but to reduce it in a remarkably efficient manner. This study should provide a template for the future of this field, where it has now been shown that through the proper manipulation of the electronic structure of main group elements that they can fix nitrogen under mild conditions. It is anticipated that future developments in ligand design may facilitate the development of more boron containing species capable of N₂ fixation, as well as the development of complexes capable of fixing nitrogen containing other p-block elements. These exciting recent results provide new insight into main group chemistry but there are still great strides that need to be taken in order for boranes (or other p-block elements) to compete with transition metals in the activation and utilization of dinitrogen.

Conflicts of interest

The authors declare that there are no conflicts of interest.

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